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Containing Strontium (Sr)

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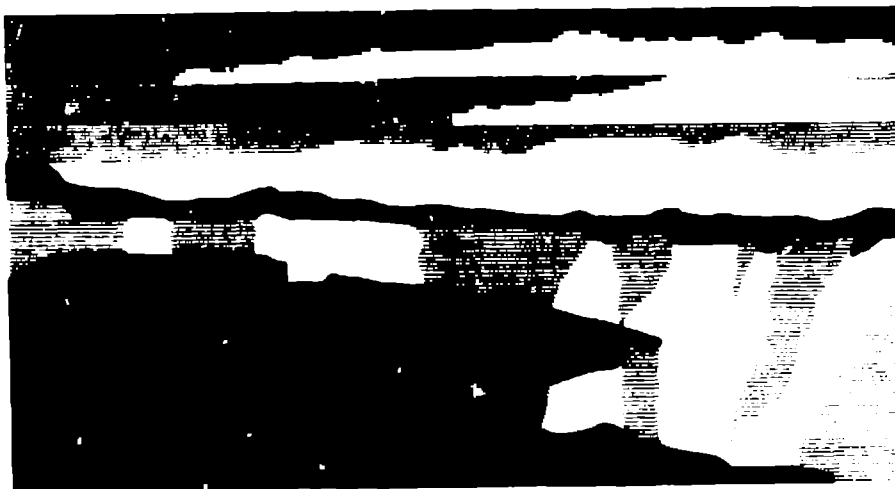
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**LASER-INDUCED BREAKDOWN SPECTROSCOPY FOR THE REAL-TIME
ANALYSIS OF MIXED WASTE SAMPLES CONTAINING Sr**

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Abstract

In this report, the use of Laser-induced breakdown spectroscopy to analyze mixed waste samples containing Sr is discussed. The mixed waste samples investigated include vitrified waste glass and contaminated soil. Compared to traditional analysis techniques, the laser-based method is fast (i. e., analysis times on the order of minutes) and essentially waste free since little or no sample preparation is required. Detection limits on the order of ppm Sr were determined. Detection limits obtained using a fiber optic cable to deliver laser pulses to soil samples containing Sr, Cr, Zr, Pb, Be, Cu, and Ni will also be discussed.

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INTRODUCTION

Nuclear reactors have been operated at government supported national laboratories for approximately fifty years. During this period, millions of gallons of mixed waste has accumulated. This waste contains fission products, transuranics, other toxic elements and compounds which are regulated by the EPA. The analysis of this type of waste by traditional analysis techniques is difficult, time consuming, and has the potential of generating significant quantities of additional waste. ^{90}Sr is typically analyzed using Gamma spectroscopy.¹ Depending upon the sample matrix, chemical and radioanalytical separation must be performed before the sample is placed in the gamma spectrometer for counting. This type of sample preparation can lead to the generation of significant quantities of additional waste. The waste issue is further compounded by the fact that ^{90}Sr is a gamma emitter requiring special sample handling procedures to ensure that the exposure of analysis personnel to gamma radiation is minimized. These types of samples must be handled, analyzed, and stored in lead lined gloveboxes or hot cells. The analysis of mixed waste samples containing Sr using gamma spectroscopy takes a minimum of hours and in many cases days or weeks.

The Laser-Induced Breakdown Spectroscopy (LIBS) technique is a relatively simple but powerful multi-elemental analysis technique requiring little sample

preparation.² In the LIBS method powerful laser pulses are focused onto the surface of a sample to generate a plasma. The emission from the plasma is then collected, wavelength dispersed, detected, and analyzed to determine the elemental composition of the sample. Since only a few nanograms to micrograms of sample is removed from the sample during the generation of the plasma and little or no sample preparation is required, this method is essentially waste free. However, for quantitative analysis, calibration curves for the elements of interest must be prepared. During this process it is possible to generate a small quantity of waste. The amount of waste generated is still much smaller than the quantity of waste generated using gamma spectroscopy. Compared to the gamma spectroscopy technique, typical analysis times for the LIBS method are on the order of minutes.

Recent results in our laboratory, indicate that a fiber optic cable can be used to deliver laser light to samples effectively for LIBS analysis. Thus, multi-element analysis can be done remotely.³ This opens up many new areas of applications of the LIBS technique. For example, the analysis of high level mixed waste in hot cells, storage tanks, gloveboxes, and other hostile environments can be performed. A fiber optic coupled LIBS system has the potential of further reducing radiation exposure to personnel who perform analytical analysis on high level mixed waste since, in principle, the analyst can be

positioned tens of meters away from the sample during analysis. This benefit has been realized because fiber optic cables are now available that allow megawatt short duration laser pulses (10 nanoseconds) to be transmitted with efficiencies greater than 99.99 % per meter without significant optical damage to the fiber.³

In this report, we will discuss results from the analysis of vitrified waste glasses and contaminated soils using the LIBS technique. The analysis of a soil sample containing Sr, Cr, Zr, Pb, Be, Cu, and Ni using a fiber optic coupled LIBS system will also be presented. The measurements on waste glasses and contaminated soils reported here were performed on nonradioactive samples containing Sr. We believe that the analysis on high level mixed waste samples will be very similar and straightforward based upon the measurements presented in this report.

EXPERIMENTAL

The LIBS technique has been described previously in detail.⁴ Thus only a brief description will be given here. A schematic of a typical LIBS apparatus is shown in Figure 1. Pulses from a Nd:Yag laser (10 nsec duration) operating at 1064 nanometers are focused onto the surface of a sample using a lens. Depending upon the sample type, laser energies from 10 to 100 mJ / pulse are used to generate the plasmas. The emission from the plasma is collected and imaged onto

the entrance slit of a spectrograph. We used 1/3-, 1/2-, or 1-meter spectrographs for the measurements presented here. The wavelength resolved emission from the spectrograph was detected with either a Tracor Northern or a Princeton Instruments 1024 element linear photodiode array detector. To obtain temporal resolution, the photodiode array detector was gated using a microchannel plate image intensifier. For the fiber optic coupled LIBS system, the output from the laser was directed into a 1.5 millimeter-diameter fiber optic using a small telescope. The output from the fiber optic cable was collimated and focused onto the surface of the sample using a pair of lenses.³ The emission was collected with a fiber optic bundle and directed onto the slit of a spectrograph. For the analysis presented in this the report, a five meter long fiber optic cable was used to transmit the laser pulses to the sample.

RESULTS AND DISCUSSION

Strontium has three strong atomic emission lines in the visible region of the optical spectrum at 407.7, 421.5, and 460.7 nm.⁵ A typical LIBS spectrum of a sample of a waste tank simulant (101-SY) is shown in Figure 2. LIBS spectra for the glass and soil samples also show Sr lines in this region.

The Sr concentration in the four glass samples (Savannah River National Laboratory) analyzed ranged between

100 and 300 ppm SrO. Concentration detection limits for the 407.7 nm emission line of Sr was determined using the 390.5 emission line of Si as an internal standard. The concentration detection limits are determined from the expression $C_L = 3 \times S / m$ where S is the standard deviation of the measurements at low concentration and m is the slope of the calibration curve.⁶ A calibration curve for Sr in the waste glass samples is shown in Figure 3. Using the data from this calibration curve, and the above expression for C_L , we obtained a detection limit of 16 ppm for Sr in the glass samples. The three S measurement corresponds to a 99.9 % level of confidence. The glass samples containing the trace amount of Sr was previously analyzed by Inductively-Coupled Plasma - Mass Spectroscopy (ICP-MS) and found to contain over 70 major and minor elements.⁷ Thus we believe that this is a clear demonstration of the ability to analyze a complex glass matrix using the LIBS technique.

Soil is another example of a complex matrix containing many elements. A LIBS spectrum of Sr in soil is shown in Figure 4 for the 407.7 nm emission line. As can be seen from the Figure, the soil blank contains a trace of Sr. For the detection limit set of measurements, the soil blank was spiked with Sr concentrations between 25 and 1000 ppm. Calibration curves for soil samples spiked with Sr are shown in Figure 5. The calculated blank concentration range between 35 and 45 ppm. We determined detection limits of 30,

24, and 80 ppm, respectively, for the 407.7, 421.5, and 460.7 nm emission lines of Sr in soil. The internal standard for this set of measurements was Fe.

We also used a fiber optic coupled LIBS system to perform measurements on soil samples. The results are shown in Table 1. It should be noted from the data presented in Table 1, that detection limits for Sr and other important metal contaminants (Cr, Sr, Pb, Be, Cu, and Ni) were determined in the sample. Although the percent relative standard deviations are high, we believe that the fiber optic LIBS system can be used to remotely analyze mixed waste samples at a distance. Investigations to improve the precision of the measurements using the fiber optic LIBS system are currently in progress. In principle, since the transmission of the laser through the fiber is 99.99 % per meter, remote analysis at distances of many meters could be performed with a high level of confidence. For example, analysis of mixed waste inside waste storage tanks, hot cells, gloveboxes, well bore holes, or other hostile environments could be performed.

CONCLUSIONS

We have demonstrated that the LIBS technique can be used to determine the elemental composition of complex mixed waste samples. Compared to traditional analysis techniques used to analyze mixed waste, this technique is simple and

analysis can be performed in a few minutes. Typical detection limits range between a few to hundreds of ppm depending upon the sample matrix and experimental conditions. This analysis technique is also essentially waste free since only a few micrograms of material is removed from the sample and little or no sample preparation is required. Using the fiber optic LIBS system, an analysts can determine the elemental composition of high level mixed waste in hot cells, storage tanks, gloveboxes, and other hostile environments. Finally, the fiber optic LIBS system has the potential of further reducing the radiation exposure to personnel who perform analytical analysis on high level mixed waste.

ACKNOWLEDGMENTS

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REFERENCES

1. W. W. Meinke and J. K. Taylor, " Analytical Chemistry: Key to Progress on National Problems ", National Bureau of Standards, Spec. Publ.351, (August 1972).

2. M. Y. Han, D. A. Cremers, and C. Y. Han, " Rapid Determination of Metal Contaminants in Soil Using the Laser Spark ", (Submitted to the International Journal of Environmental Chemistry).
3. D. A. Cremers, J. E. Barefield II, and A. C. Koskelo, " Remote Elemental Analysis by Laser-Induced Breakdown Spectroscopy Using a Fiber Optic Cable ", Accepted for publication in Appl. Spectrosc. (1995).
4. D. A. Cremers and L. J. Radziemski, " Laser Plasmas for Chemical Analysis ", in Laser Spectroscopy and Its Applications, (L. J. Radziemski, R. W. Solar, and J. A. Pasiner, eds., Marcel Dekker, New York, 1986), chap. 7, pp 351-415.
5. J. Reader and C. H. Corlis, " Wavelengths and Transition Probabilities for Atoms and Atomic Ions ", National Standard Reference Data Systems - National Bureau of Standards (NSRDS-NBS, 68), Part 1, Washington, D. C., (1930).
6. H. Kaiser, " Two Papers on the Limit of Detection of a Complete Analytical Procedure ", (Hafner Publishing Company, Inc., New York, N. Y., 1968).
7. C. J. Coleman, " Defense Waste Process Facility (DWPF) Analytical Procedures ", (Westinghouse Savannah River Company, Aiken, S. C., 1988), DPST-88-270.

Table 1. LIBS Detection Limits Obtained Using Fiber Optic Delivery of Laser Pulses¹

Analyte/Wavelength(nm)	Reference/Wavelength(nm)	C _L (ppm)	% RSD ²
Sr(I) / 407.77	Fe(I) / 407.17	13	17
Cr(I) / 427.48	Fe(I) / 432.57	54	29
Cr(I) / 432.57	Fe(I) / 357.01	48	23
Zr(I) / 343.82	Fe(I) / 346.59	65	20
Pb(I) / 405.78	Fe(I) / 407.17	106	35
Be(II) / 313.1	Ca(I) / 317.93	3	19
Cu(I) / 327.39	Ti(I) / 326.16	48	33
Ni(I) / 341.47	Fe(I) / 346.59	114	41

¹Each measurement obtained by averaging 100 laser pulses.

² Average %RSD of five lowest measured concentrations used to compute C_L.

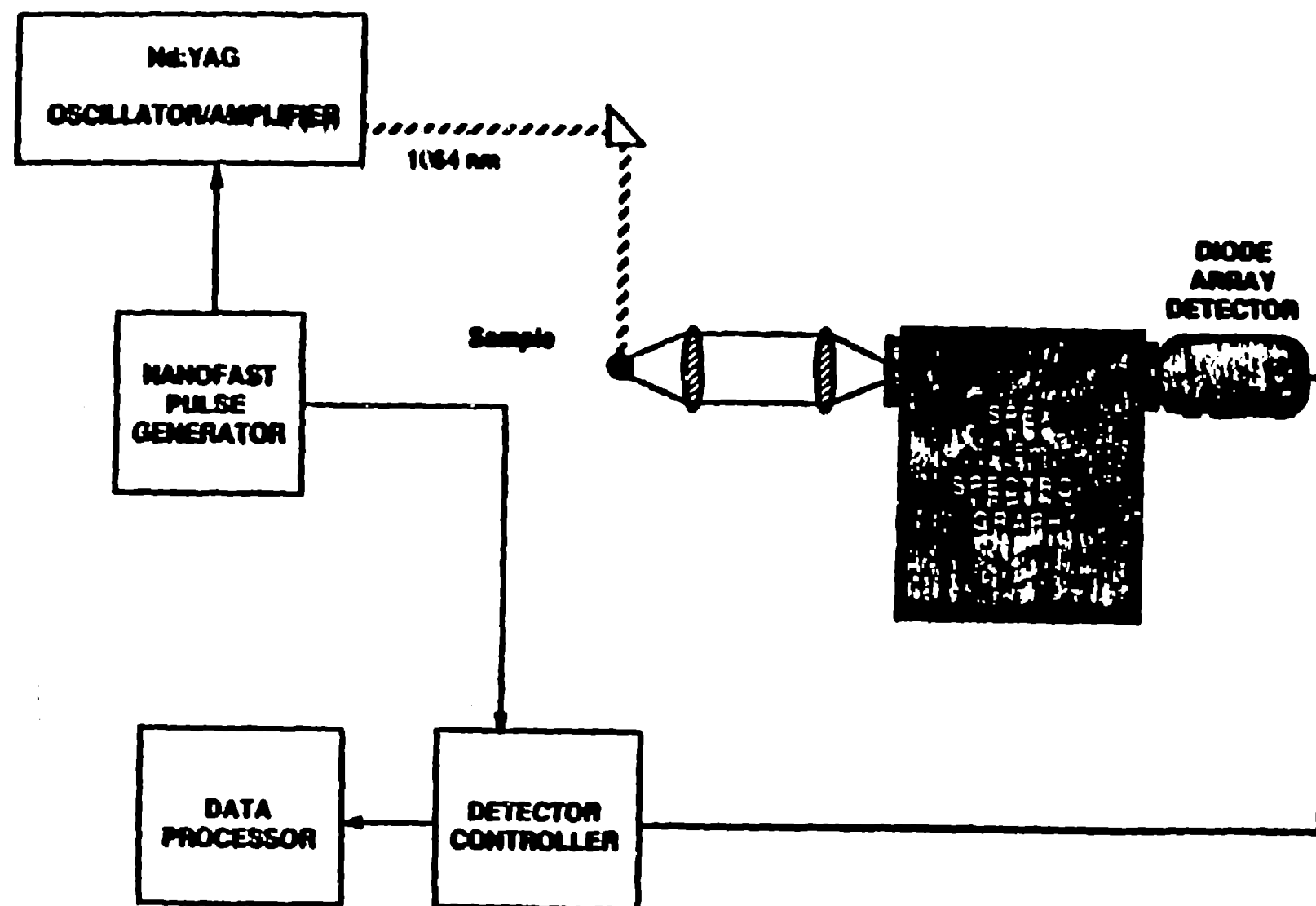


Figure 1. Laser induced breakdown spectroscopy apparatus.

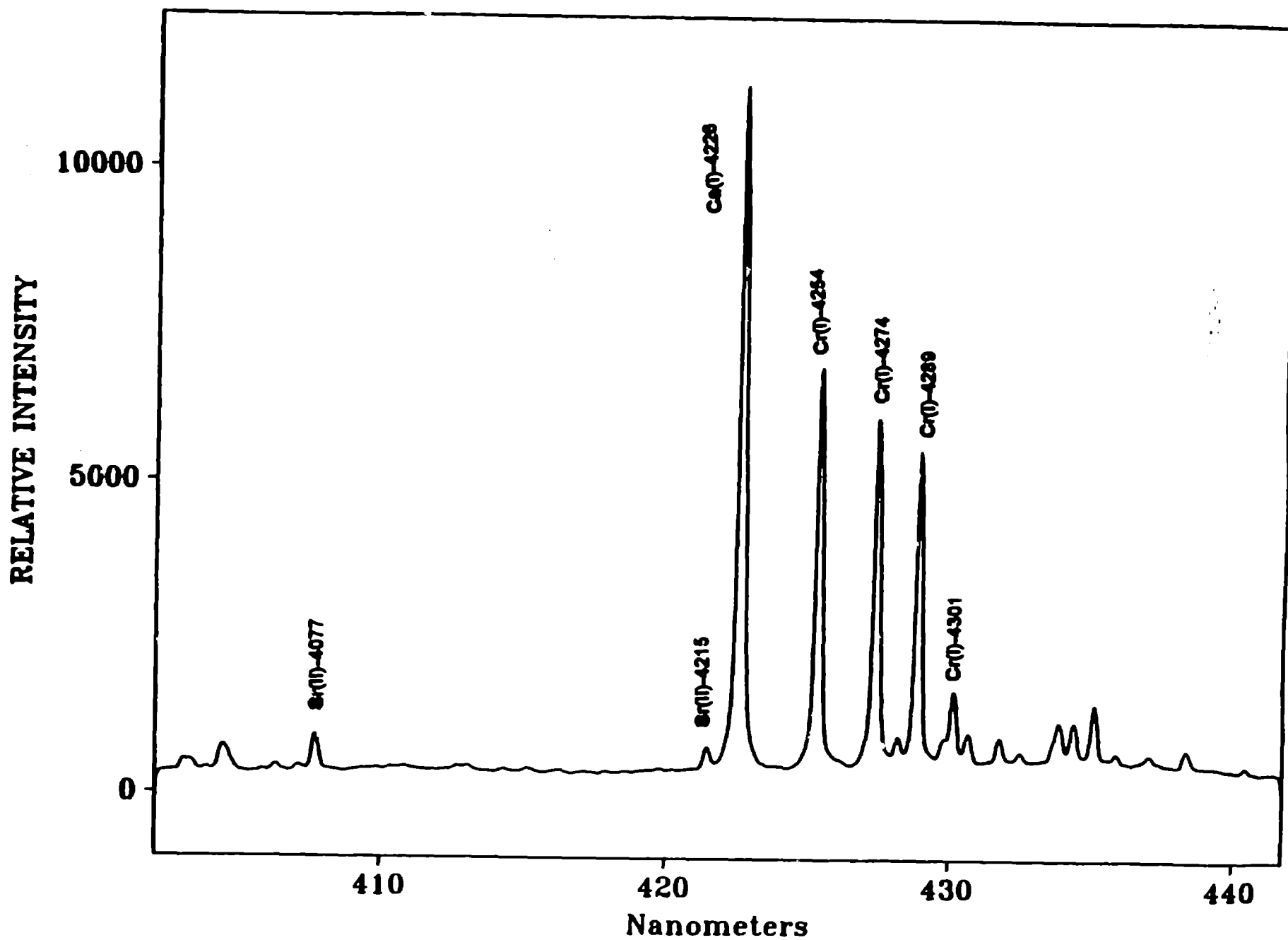


Figure 2. A LIBS spectrum of a sample of waste tank simulants in the 420 nanometer region.

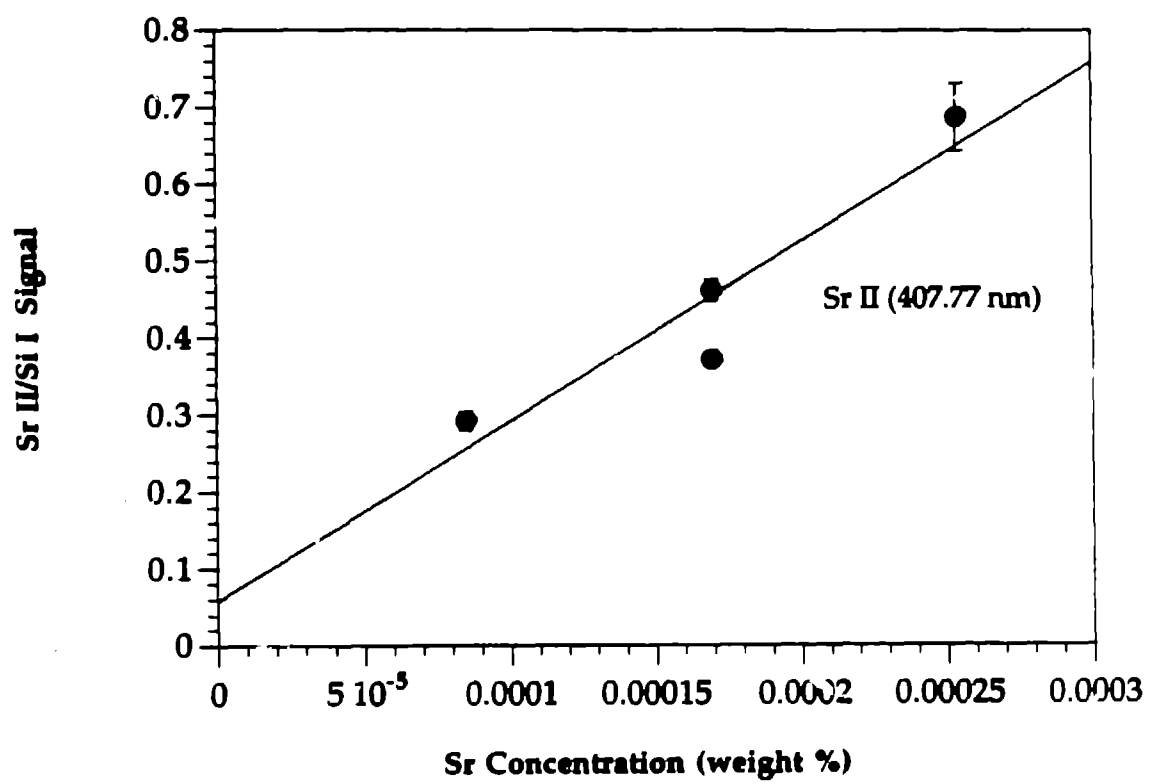


Figure 3. A calibration curve for the concentration of Sr in waste glass samples.

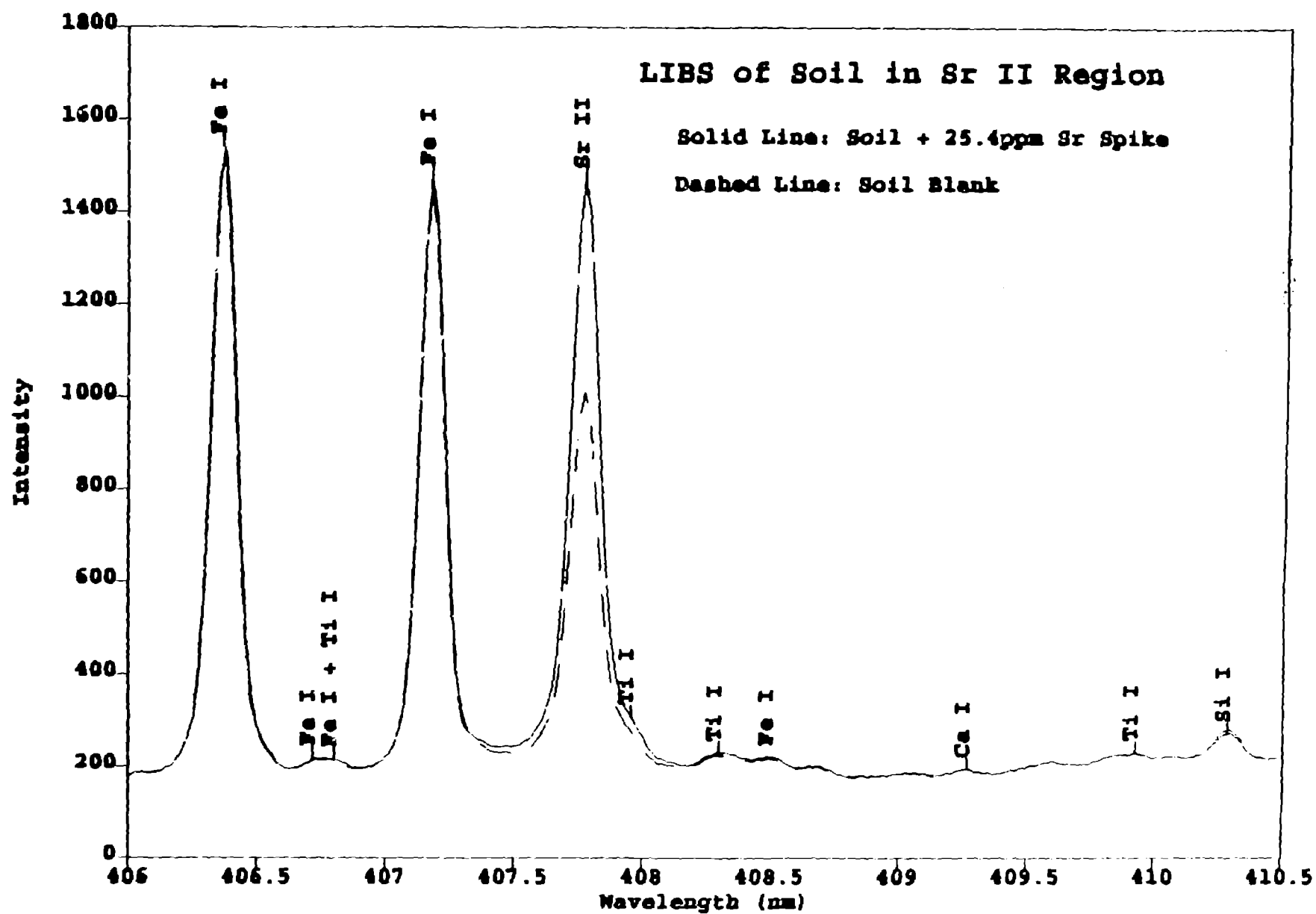


Figure 4. A LIBS spectrum of Sr in soil in the 400 nanometer region.

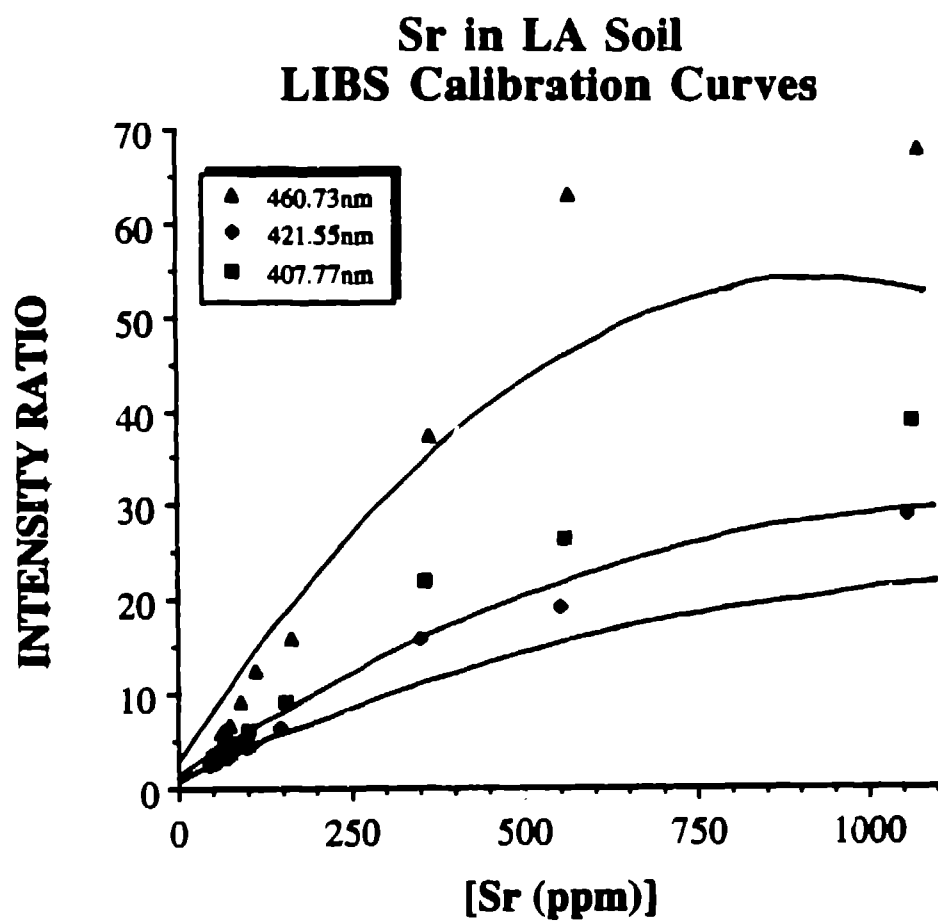


Figure 5. Calibration curves for Los Alamos soil samples spiked with Sr.